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(71) Applicant:
NIPPON SHEET GLASS CO. LTD.
Chuo-ku Osaka-shi Osaka-fu (JP)

(72) Inventors:
- **Seto, Hiromitsu,**
  c/o NIPPON SHEET GLASS Co., Ltd.
  Osaka-Shi, Osaka (JP)
- **Nagashima, Yukihito**
  Nishinomiya-shi, Hyogo (JP)
- **Yoshii, Shigekazu**
  Hyogo (JP)

(74) Representative:
Grünecker, Kinkeldey,
Stockmair & Schwanhäusser
Anwaltssozietät
Maximilianstrasse 58
80538 München (DE)

(54) Ultraviolet/infrared absorbent low transmittance glass

(57) The ultraviolet/infrared absorbent low transmittance glass has a greenish almost neutral color, middle visible light transmittance, low total solar energy transmittance, and low ultraviolet transmittance, and is suitable for a window of a vehicle or a building and capable of preventing degradation and discoloration of interior materials and protecting privacy. The glass consists of base glass comprising: 65 to 80 wt. % SiO_2; 0 to 5 wt. % Al_2O_3; 0 to 10 wt. % MgO; 5 to 15 wt. % CaO (within such a range that a total amount of MgO and CaO becomes 5 to 15 wt. %); 10 to 20 wt. % Na_2O; 0 to 5 wt. % K_2O (within such a range that a total amount of Na_2O and K_2O becomes 10 to 20 wt. %); and 0 to 5 wt. % B_2O_3, and colorants including: 0.7 to 0.95 wt. % total iron oxide (T-Fe_2O_3) converted to Fe_2O_3; 1.1 to 2.3% TiO_2, 0 to 2.0% CeO_2, 0.013 to 0.025 wt. % CoO; 0 to 0.0008 % Se; and 0.01 to 0.07 % NiO. A visible light transmittance (YA) in a range from 25% to 45% and a total solar energy transmittance is in a range from 10% to 40% at a thickness between 3.1 and 5 mm.

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Description

BACKGROUND OF THE INVENTION AND RELATED ART STATEMENT

The present invention relates to an ultraviolet/infrared absorbent low transmittance glass. More particularly, it relates to an ultraviolet/infrared absorbent low transmittance glass which has a greenish almost neutral color, middle level of visible light transmittance, low total solar energy transmittance, and low ultraviolet transmittance so that it is suitable for use as privacy glazing of a vehicle.

Recently, a variety of glass with ultraviolet/infrared absorbability to be used as a vehicle windshield has been proposed with the view of preventing degradation of luxurious interior materials and reducing cooling load of the vehicle. In view of privacy protection, glass with relatively low visible light transmittance is preferably used for a rear window glass of a vehicle. Such kinds of glass include the followings.

A dark gray colored glass disclosed in Japanese Patent Publication JPA 8-157232 consists of soda-lime-silica glass including colorants consisting of 0.8 to 1.4 weight percent Fe_2O_3 (total iron), less than 0.21 weight percent FeO, 0.05 to 1.0 weight percent TiO_2, 0.02 to 0.05 weight percent CoO, and 0.0005 to 0.015 weight percent Se.

A neutral gray colored glass disclosed in claim 25 of U. S. Patent No. 5,393,593 has a base glass composition comprising colorants consisting of 1.00 to 2.2 weight percent Fe_2O_3 (total iron), at least 0.20 weight percent FeO, 0.0005 to 0.005 weight percent Se, and 0.010 to 0.030 weight percent CoO. The glass exhibits luminous transmittance less than 35 percent and total solar infrared transmittance less than 20 percent at 3.9 mm thickness.

A gray colored soda-lime-silica glass disclosed in JPA 8-67526 comprises colarants consisting of 0.15 to 1.2 weight percent Fe_2O_3(total iron), less than 0.3 weight percent of FeO, 60 to 180 ppm CoO, 0 to 30 ppm Se, and 0 to 550 ppm NiO, which has luminous transmittance from 20 to 50 percent at a thickness of 3.9mm.

The dark gray colored glass disclosed in JPA 8-157232 is unpreferable because the luminous transmittance thereof is too low.

The neutral gray colored glass disclosed in U.S. Patent No. 5,393,593 is also unpreferable because of its low luminous transmittance and the great content of CoO and Se.

The aforementioned glass with low visible light transmittance is superior in privacy protection, but they are unpreferable in that an occupant in a vehicle cabin sees outside quite unclearly through the glass and that a high mount stop lamp is seen unclearly. A glass with middle transmittance has been required for satisfying both privacy protection and traffic safety.

The aforementioned glass includes selenium in high concentration to provide optical properties, without essentially including nickel.

Selenium is necessary to be added to a glass batch in an amount ten times as much as demanded quantitiy in the batch, since nearly 90% of the selenium added is vaporized. Such large additive amount of selenium is unpreferable for preventing environmental polution because of its severe toxicity.

The above glass has many difficulties in being melted in an ordinary glass melting tank. because the glass comprises FeO(T-Fe_2O_3) in a large amount so that it radiates heat rays strongly to heat a crown of the melting tank higher than its refractory temperature.

The gray glass composition disclosed in JPA 8-67526 has high ultraviolet transmittance higher than 10% as described in the example thereof, and the glass is unpreferable for protecting degradation of interior materials and for comfortable driving of a car.

OBJECT AND SUMMARY OF THE INVENTION

It is an object of the present invention to provide an ultraviolet/infra red absorbent low transmittance glass which has a greenish almost neutral color, which has middle visible light transmittance, low ultraviolet transmittance, and low total solar energy transmittance and which is produced easily with using a normal glass melting tank.

The ultraviolet/infrared absorbent low transmittance glass of the present invention consists of a base glass, that is, the major constituents comprising:

65 to 80 wt. % SiO_2;
0 to 5 wt. % Al_2O_3;
0 to 10 wt. % MgO;
5 to 15 wt. % CaO (within such a range that total amount of MgO and CaO becomes 5 to 15 wt. %);
10 to 18 wt. % Na_2O;
0 to 5 wt. % K_2O (within such a range that total amount of Na_2O and K_2O becomes 10 to 20 wt. %); and
0 to 5 wt. % B_2O_3,

and a colorant including:

0.7 to 0.95 wt. % total iron oxide (T-Fe_2O_3) converted to Fe_2O_3;
1.1 to 2.3 wt. % TiO_2;
0 to 2.0 wt. % CeO_2;
0.013 to 0.025 wt. % CoO;
0 to 0.0008 % Se; and
0.01 to 0.07 % NiO.

The glass of the present invention preferably exhibits ultraviolet transmittance, defined by ISO 9050, less than 10% at a thickness between 3.1 mm and 5 mm.

When measured using C.I.E. standard illuminant "C" over the wavelength range 380 to 770 nanometers, the glass of the present invention preferably has optical properties with dominant wavelengths in the range of 480 to 560 and excitation purity less than 10% at a thickness between 3.1 mm and 5 mm.

PREFERRED EMBODIMENTS

The description will be made as regard to an ultraviolet/infrared absorbent low transmittance glass composition. It should be noted that components will be represented with percentage by weight.

SiO_2 (silica) is a principal component for forming skeleton of glass. Less than 65% SiO_2 lowers the durability of the glass and more than 80% SiO_2 raises the melting temperature of the glass so high.

Al_2O_3 is a component for improving the durability of the glass. More than 5% Al_2O_3 raises the melting temperature of the glass so high. The preferable range of Al_2O_3 is between 0.1% and 2%.

MgO and CaO improve the durability of the glass and adjust a devitrification temperature and viscosity of the glass during molding. More than 10% MgO raises the devitrification temperature. Less than 5% or more than 15% CaO raises the devitrification temperature of the glass. The durability of the glass is lowered when the total amount of MgO and CaO is less than 5%, while the devitrification temperature is increased when the total exceeds 15%.

Na_2O and K_2O prompt the glass to melt. The efficiency of promotion of melting becomes poor when Na_2O is less than 10% or the total of Na_2O and K_2O is less than 10%, while the durability of the glass is lowered when Na_2O exceeds 18% or the total of Na_2O and K_2O exceeds 20%. K_2O is preferable not to exceed 5% because of its expensive cost.

B_2O_3 is a component for improving the durability of the glass, prompting to melt, and yet enhancing the ultraviolet absorption. B_2O_3 should be less than 5%, since the transmittance is reduced also at a visible range so that the color of the glass is easy to tint yellow and difficulties during molding are caused due to the vaporization of B_2O_3 when B_2O_3 exceeds 5%.

Iron oxide is present in the form of Fe_2O_3 and the form of FeO in the glass. Fe_2O_3 is a component for improving the ultraviolet absorptivity and FeO is a component for improving the heat ray absorptivity.

When the amount of FeO is too little, the heat ray absorptivity becomes small. When the glass comprises too much FeO, the luminous transmittnace of the glass becomes lower than an ordinary level. In addition when the glass comprises too much FeO, there is an unpreferable possibility that the temperature around a crown of a glass melting furnace exceeds its refractory temperature due to absorption of the heat ray by the ferrous oxide. When an amount of FeO converted to Fe_2O_3 is from 0.15% to 0.40%, the glass has a middle level of the luminous transmittance and is supreme in heat ray absorptivity.

When T-Fe_2O_3 is less than 0.7%, the glass is inferior in both of ultraviolet and infrared absorptivity. When T-Fe_2O_3 exceeds 0.95%, the amount of FeO tends to become high and the glass becomes hard to be melted in an ordinary glass melting furnace.

TiO_2 is a component for improving the ultraviolet absorptivity particularly by interaction with FeO. In case TiO_2 is added with NiO, the excitation purity of the glass is reduced and the color of the glass becomes neutral color such as green. When TiO_2 is less than 1.1%, the ultraviolet absorptivity becomes inadequate, and the glass becomes bluish unfavorably to have high exciting purity. When TiO_2 exceeds 2.3%, the glass becomes yellowish unpreferably.

CeO_2 is a component for improving the ultraviolet absorptivity and is present in the form of Ce^{3+} or in the form of Ce^{4+} in glass. Ce^{3+} is effective in absorbing ultraviolet with less absorptivity in the visible range. When CeO_2 and TiO_2 coexist in the glass, ultraviolet is absorbed also by interaction of Ce^{3+} and Ti^{4+} . CeO_2 is preferably contained in an mount of less than 2% so as to have greenish neutral color and to reduce the cost of expensive CeO_2.

CoO is a component for forming an almost greenish neutral color by cooperating with NiO and/or Se, and Fe_2O_3 as well as TiO_2. Less than 0.013% CoO makes the visible light transmittance too high. More than 0.025% CoO makes the color of too blue tint and reduces the visible light transmittance. CoO is comprised preferably in an amount from 0.019 to 0.025%.

Se(selenium) contributes a pink color, so that it reduces the excitation purity with the aid of a complementary color

of CoO. More than 0.0008% Se reduces the visible light transmittance and is unpreferable for preventing environmental polution. It should be noted that Se may not comprised as a colorant in the glass of the present invention.

NiO is a component for controlling the visible light transmittance and for reducing the excitation purity. NiO is preferably contained in an amount not less than 0.01%. When NiO is more than 0.07%, nickel sulfide stones or colored bubbles comprising nickel sulfide are sometimes present in the product and the visible light transmittance is reduced. The content of NiO is preferably in a range between 0.03% and 0.06%.

The nickel sulfide stones or the colored bubbles comprising nickel sulfide should be as little as possible. To prevent the formation of nickel sulfide stones, ZnO may be added in a range less than 0.5%. Expensive ZnO of more than 0.5% will push up a batch cost. ZnO is added preferably in a form of zinc sulfate($ZnSO_4$ or $ZnSO_4 \cdot 7H_2O$) or zinc nitrate($Zn(NO_3)_2 \cdot 6H_2O$). ZnO is added more preferably in an amont from 0.01 to 0.3%.

One or more than two among MnO, V_2O_5, MoO_3, CuO, Cr_2O_3, and SnO_2 may be added within a rang from 0% to 1% in total as a colorant or a reducing agent in such a range as not to lose middle transmittance and the almost neutral color nearly green.

[Examples]

Hereinafter, the mode of carrying out the present invention will be described referring to examples.

(Examples 1 through 19)

Glass raw material is prepared by adding at least one of a group consisting of ferric oxide, titanium oxide, cerium oxide, cobalt oxide, metallic selenium, nickel oxide, zinc sulfate, and a carbonaceous reducing agent into a standard soda-lime-silica glass batch composition, and mixing them. The batch composition consists of

SiO_2	72.4%,
Al_2O_3	1.6 %,
MgO	3.6%,
CaO	8.4%,
Na_2O	13.1%, and
K_2O	0.9%,

The glass raw material thus prepared is heated and melted in an electric furnace at 1500 °C for 4 hours. The molten glass is flowed onto a stainless plate and annealed to the room temperature to obtain a 6 mm thick glass plate. The glass plate is then polished in such a manner that the thickness reduces to 4 mm to become a sample. Each sample is measured in the visible light transmittance (YA) by the C.I.E illuminant A, the total solar energy transmittance (TG), the ultraviolet transmittance by ISO 9050(TUV), the dominant wavelength (DW) by the illuminant C, and the excitation purity (Pe).

Tables 1 and 2 also show T-Fe_2O_3 concentration FeO (converted to Fe_2O_3) / T-Fe_2O_3 rate, CoO concentration, Se concentration, NiO concentration, CeO_2 concentration, and TiO_2 concentration The numerals in Tables are indicated as a percentage of the weight. Tables 1 and 2 also show the optical properties of the respective samples.

All of the samples of Examples 1 through 19 are within the scope of the present invention and exhibit excellent optical properties.

It is shown that Examples 2 and 8-18 have low exitation purity because of rich CoO concentration thereof.

Examples 2 to 18 show that exitation purity is reduced by NiO. Each glass of Examples 4 to 18 is given excellent optical properties by a proper amount of NiO in spite Se is not comprised.

Example 19 is added CuO in order to reduce the total solar ultraviolet transmittance, and can exhibit high infrared absorptivity without losing the visible light transmittance and the ultraviolet absorptivity.

Each glass of the examples is suitable for a rear window of a vehicle, a window of a building, and the like which prevent degradation of interior materials and is useful for trafic safety..

(Examples 20 through 23)

Glass samples are prepared in a same manner as in the examples 1 to 19 except that only NiO is added in the

example 20, and both of NiO and zinc sulfate are added in the examples 21 to 23 to the glass batch of the Examples 1 to 19. Each number of NiS particles formed in the sample glass is shown in Table 3.

Table 3 shows that the number of NiS is extremely smaller in the examples 21 to 23 where ZnO is comprised than in the example 20.

(Comparative Examples 1-4)

Table 4 shows glass components and optical properties of Comparative Examples.

All of Comparative Examples 1-4 have components out of the scope of the present invention Comparative Example 1 has the same components as the example of the JPA 8-157232 as referred above and Comparative Example 2 has the same components as the example of U. S. Patent No. 5,393,593 as referred above. Comparative Example 3 contains TiO_2 as a colorant of which amount is out of the scope of the present invention Comparative Example 4 contains T-Fe_2O_3, CoO and TiO_2, each amount of which is out of the scope of the present invention. It should be noted that the optical properties of Comparative Example 1 are indicated in values based on a glass thickness of 5 mm and the optical properties of Comparative Example 2 are indicated in values based on a glass thickness of 3.9 mm.

It is apparent from Table 4 that the Comparative Example 1 has smaller values of visible light transmittance and total solar energy transmittance than the Examples of the present invention, Comparative Example 2 has visible light transmittance and total solar energy transmittance, as high as the Examples of the present invention, but it has lower ultraviolet transmittance. Comparative Example 3 has too high values in exciting purity and ultraviolet transmittance. Comparative Example 4 has a too high exciting purity value.

As detailed above, the glass of the present invention exhibits middle visible light transmittance, low total solar energy transmittance, and low ultraviolet transmittance and which has a greenish almost neutral color.

The ultraviolet/infrared absorbent low transmittance glass prevents degradation and discoloration of interior materials and protects privacy when the glass is used for a rear window glass of a vehicle, a window of a building, or the like.

[Table 1]

Example No. / (wt%)	1	2	3	4	5	6	7	8	9	10
T-Fe$_2$O$_3$	0.8	0.9	0.8	0.8	0.9	0.96	0.9	0.8	0.8	0.8
FeO/T-Fe$_2$O$_3$	23.8	18.9	25.0	23.1	22.2	30.0	22.1	27.6	27.0	27.9
NiO	0.01	0.03	0.035	0.04	0.06	0.04	0.04	0.035	0.03	0.035
Se	0.0008	0.0005	0.0003	—	—	—	—	—	—	—
CoO	0.018	0.019	0.013	0.018	0.017	0.0185	0.013	0.019	0.019	0.021
TiO$_2$	2.1	1.5	1.1	1.2	1.7	1.1	1.1	1.7	2.3	1.8
CeO$_2$	—	0.5	—	—	—	—	1.0	—	—	—
YA (%)	25.4	30.4	37.4	34.7	29.0	29.1	36.6	31.3	30.6	28.9
TG (%)	25.6	29.3	32.2	31.2	27.5	26.7	30.6	29.0	26.5	27.9
DW (nm)	525	550	529	491	547	489	543	492	511	490
Pe (%)	9.8	5.0	1.7	4.6	6.8	9.5	3.6	8.3	4.3	8.6
Tuv (%)	5.0	5.0	6.3	6.3	6.9	7.8	3.1	7.8	4.2	7.5

[Table 2]

Example No. / (wt%)	11	12	13	14	15	16	17	18	19
T-Fe$_2$O$_3$	0.8	0.8	0.85	0.9	0.9	0.7	0.8	0.8	0.8
FeO/T-Fe$_2$O$_3$	23.8	23.8	25.9	33.3	22.5	21.4	21.0	23.8	23.5
NiO	0.04	0.045	0.04	0.04	0.06	0.04	0.04	0.04	0.04
Se	—	—	—	—	—	—	—	—	—
CoO	0.019	0.019	0.019	0.019	0.019	0.019	0.024	0.019	0.017
TiO$_2$	1.7	1.7	2.1	1.6	1.6	1.1	1.1	1.1	1.2
CeO$_2$	—	—	—	—	—	2.0	1.0	1.5	CuO:0.2
YA (%)	30.9	30.1	27	25.7	27.1	31.6	25.7	30.0	29.7
TG (%)	29.6	29.3	25.3	19.8	26.9	34.0	30.0	29.0	27.6
DW (nm)	495	496	495	492	519	493	484	492	493
Pe (%)	6.8	6.1	5.9	9.4	3.8	6.6	8.8	7.5	7.7
Tuv (%)	7.8	8.3	5.1	5.2	7.4	2.2	4.0	2.5	7.3

[Table 3]

Example No.	20	21	22	23
Nio concentration (%)	0.04	0.04	0.06	0.06
ZnO concentration (%)	—	0.01	0.15	0.3
numbers of particles of NiS (numbers/g)	0.6	0.4	0.3	0.1

[Table 4]

Comparative Example No. (wt%)	1	2	3	4
T-Fe_2O_3	0.82	1.06	0.8	1.3
FeO/T-Fe_2O_3	12.2	35.2	23.0	28.0
NiO	—	—	0.02	0.011
Se	0.0105	0.00103	—	—
CoO	0.0283	0.0123	0.019	0.012
TiO_2	0.80	—	1.00	0.03
thickness (mm)	5.0	3.9	4.0	4.0
YA (%)	23.5	32.6	35.3	36.8
TG (%)	9.0	21.0	32.9	22.5
DW (nm)	576	488	485	487
Pe (%)	2.8	7.4	14.7	15.5
Tuv (%)	3.2	17.4	11.0	7.1

Claims

1. An ultraviolet/infrared absorbent low transmittance glass consisting of base glass comprising:

65 to 80 wt. % SiO_2;
0 to 5 wt % Al_2O_3;
0 to 10 wt. % MgO;
5 to 15 wt. % CaO (within such a range that the total amount of MgO and CaO becomes 5 to 15 wt. %);
10 to 18 wt. % Na_2O;
0 to 5 wt. % K_2O (within such a range that the total amount of Na_2O and K_2O becomes 10 to 20 wt. %); and
0 to 5 wt. % B_2O_3,

and colorants comprising:

0.7 to 0.95 wt. % total iron oxide (T-Fe_2O_3) converted to Fe_2O_3;
1.1 to 2.3 wt. %TiO_2;
0 to 2.0 wt. % CeO_2;
0.013 to 0.025 wt. % CoO;
0 to 0.0008 % Se; and
0.01 to 0.07 % NiO.

said glass having a visible light transmittance (YA) by the C.I.E. illuminant A respectively in a rang from 25% to 45% and a total solar energy transmittance (TG) in a range from 10% to 40% at a thickness between 3.1 and 5 mm.

2. An ultraviolet/infrared absorbent low transmittance glass as claimed in claim 1, wherein CoO is between 0.019 wt. % to 0.025 wt. %.

3. An ultraviolet/infrared absorbent low transmittance glass as claimed in claim 1 or 2, wherein NiO is between 0.03 wt. % to 0.06 wt. %.

4. An ultraviolet/infrared absorbent low transmittance glass as claimed in any of claims 1 to 3, wherein Se is not substantially comprised.

5. An ultraviolet/infrared absorbent low transmittance glass as claimed in any of claims 1 to 4. wherein said glass has an ultraviolet transmittance, defined by ISO, of no greater than 10% at a thickness of said glass between 3.1 and 5 mm.

6. An ultraviolet/infrared absorbent low transmittance glass as claimed in any of claims 1 to 5, wherein the dominant wavelength of the glass is in the range of 480 to 560 nanometers and the excitation purity of the glass is less than 10% when the measurement is made based on a glass thickness between 3.1 and 5 mm with using illuminant C.

7. An ultraviolet/infrared absorbent low transmittance glass as claimed in any of claims 1 to 6, wherein ZnO is between 0 to 0.5 wt. %.

8. An ultraviolet/infrared absorbent low transmittance glass as claimed in any of claims 1 to 7, wherein ZnO is between 0.01 wt. % to 0.3 wt. %.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 11 8636

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A D	EP 0 653 388 A (PPG INDUSTRIES INC) 17 May 1995 * page 2, line 37 - page 3, line 40; tables * & JP 08 067 526 A	1-8	C03C3/087 C03C3/095 C03C4/02 C03C4/08
A	US 5 411 922 A (JONES JAMES V) 2 May 1995 * column 2, line 33 - line 61 * * column 4, line 7 - line 24 *	1-8	
A	PATENT ABSTRACTS OF JAPAN vol. 018, no. 639 (C-1282), 6 December 1994 -& JP 06 247740 A (CENTRAL GLASS CO LTD), 6 September 1994, * abstract *	1-8	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)
C03C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	12 February 1998	Van Bommel, L

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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